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JOURNAL ARTICLE

Oxidative Treatment of Industrial Wastewater

by Fred Ellerbusch & Herbert S. Skovronek

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Mr. Fred Ellerbusch is an environmental engineer who recently joined the Mitre Corporation in McLean, Virginia after several years employment in EPA's Industrial Pollution Control program. While with the EPA, Mr. Ellerbusch was responsible for developing and evaluating improved pollution control technology for several industrial areas, including plastics, synthetic rubber and several specialty chemicals.

Abstract

Using a somewhat unusual approach this paper defines industrial waste treatment process as falling into categories of oxidative destruction, reductive destruction, and non-destructive, separation operations.

The various oxidative approaches, including biological, chemical and thermal methods, are then discussed in detail in this first paper of a series. Advantages, disadvantages and generalized cost comparisons are presented. U.S. EPA sponsored projects are identified, where possible, as examples of the various technologies which can be referred to by the reader. The paper attempts to alert the reader to the wide range of oxidative processes that can be used as part of a composite pollution abatement system and to the advantages and limitations of these techniques.

Introduction

Over the past ten to fifteen years industrial wastewater treatment has evolved to a much more sophisticated and prominent status as the nation has recognized the need to control more and more complex mixtures of pollutants. From an initial thrust mandated by PL 500[1] and the preceding Water Pollution Laws oriented primarily toward BOD, SS and, occasionally, COD and specific pollutant control, the program is now turning toward much greater attention to specific pollutant and toxic pollutant control in reply to a recent Consent Degree,[2] a Toxic Substance Law[3] passed by the 94th Congress and a Drinking Water Law[4] all responding to well publicized concern over potentially toxic and carcinogenic pollutants. Simultaneously, technology for achieving adequate elimination or control of such pollutants has developed from the basic biological degradation systems to highly sophisticated, specific unit operations and processes.

Technology needs can be divided into two basic categories: Destructive and non-destructive. Destructive methods may be further divided into oxidative, reductive and thermal techniques. Non-destructive routes, potentially allowing recovery of resources, would include membrane techniques, absorption, extraction, ion exchange, etc. This paper will review and survey only oxidative destruction methods, which constitute a major segment of those in use, while future papers in this series will address other treatment classes.

Oxidation of wastewater pollutants is the major mechanism by which pollutants are controlled today and has been demonstrated to occur by a variety of biological, chemical, and physical-chemical processes. Those to be examined in this paper will include:

Biological processes such as:

Activated sludge, trickling filter, UNOX®, oxidation ditch, aerated lagoon, rotating biological systems.

Chemical processes:

Ozone, air (catalytic and non-catalytic), electrochemical, peroxide, permanganate.

Thermal:

Wet oxidation, incineration.

Although arbitrary, the distinction between biological, chemical and thermal is used to facilitate the discussion of these topics. Thermal processes could equally well be incorporated under chemical oxidative processes using air as the oxidant. Pyrolysis, a non-oxidative process, is excluded from this discussion.

Oxidative destruction, whether by biological, chemical, or thermal processes is applicable to a wide range of organic and inorganic pollutants. It offers the opportunity to destroy organic pollutants partially or totally, and to change toxicity of the waste — usually towards reduced levels, as molecular complexity is decreased. Consequently, increased bioreactivity often results. Concomitantly, solubility in aqueous media would usually be increased, and thus, bioassimilation would be apt to increase. Assuming that both changes are occurring simultaneously, the ease of biodegradation, either in a waste treat-

ment system or in the natural environment, tends to improve. The reader should bear in mind that the foregoing are general statements and that there are numerous exceptions in the real world.

The advantages of oxidative removal destruction of pollutants often must be weighed against actual or potential disadvantages. For example, toxicity could increase by increased solubilization. Or, if a total treatment system includes a physical treatment step such as carbon adsorption, adsorbability of the wastes could decrease by virtue of oxidative changes to more soluble species. And, finally, where oxidation is achieved by thermal or chemical methods, cost and energy requirements may become excessive.

The EPA has supported numerous studies in many of these areas in an effort to develop improved, more selective or more cost-effective treatment technology; many of these projects will be used as examples. The reader is urged to seek more detailed information from the specific references.

Biological Oxidation

Several oxidative biological degradation schemes have evolved or been developed over the past decades. Of these the most commonly used, both for municipal and for industrial wastes, is activated sludge. All aerobic biological treatment systems are, in reality, oxidative processes. Just as human metabolism of food is a very complex oxidation system — so too is the conversion of organic pollutants in wastewater to carbon dioxide an oxidative process, the active ingredient being oxygen from the air and the biota serving as the "reactor" and frequently, as the source of unique catalysts, e.g., enzymes.

Aerobic biological systems are designed for removal of generalized measurable parameters such as BOD, and do not take into account chemical reactivities of different components, the extreme being the non-reactive or highly refractory species. Supplemental nutrients such as phosphorus, nitrogen and trace elements must be present to allow the biota to carry out the intermediate metabolic processes which culminate in the reproduction of the biota and generation of carbon dioxide and water. The introduction of oxygen or air by mechanical aeration or injection continues as a major research effort to minimize the significance of oxygen mass transfer as the rate controlling step.

Biological systems remain one of, if not the most cost-effective treatment methods for many wastes, even those containing a wide array of complex organic chemicals. Introduced in the early 1900's for sanitary waste treatment, various biological systems have been adapted (with varying degrees of success) over the past decades to the treatment of complex industrial wastes. Sensitivity to sudden changes in waste load (either quality or quantity) is high and variable. Careless introduction of toxic chemicals, which might otherwise have been assimilated, or the presence of specific toxicants, can severely affect operation. In most cases, land requirements are large by process standards since successful vertical systems have not yet been developed and demonstrated for industrial wastes. Sludges, often containing metals and absorbed organics which remain toxic or hazardous, must be dewatered and disposed of. Rate dependence on ambient temperature is great enough to cause major seasonal changes in the effectiveness of operation across a significant portion of the country. And finally, reliance on BOD removal, while adequate for sanitary wastes, is often totally fallacious with industrial wastes.

Biological treatment as it is currently practiced is highly cost-effective. Particularly where the availability and cost of land are not major factors, biological treatment continues to be one of the most economical means of removing biodegradable pollutants from a process or plant wastewater stream. It has often been noted that; "the bugs work for free." Other than land costs, the only major cost item is usually the hardware for air or oxygen introduction. (Table I,

EPA has carried out numerous studies of various biological systems over the past years to demonstrate the viability of biological treatment for diverse, complex industrial wastes, particularly to determine the utility of this group of processes to treat industrial discharges and meet regulations such as those imposed by the BPT requirements of PL-500. Table II presents summaries of these studies. Although surprisingly adaptable, in some cases the systems have not performed well due to the nature or load of the pollutants in the wastewater, local weather conditions, or other unanticipated factors. As with all treatment systems, the ingenuity of the design engineer often can contribute significantly to the success of the project. And, of course, a primary point to bear in mind is that a biological system can only eliminate those chemical species which are biodegradable during the given detention time. With certain plastic manufacturing wastes it has found that lagoon detention times as long as one half year were being

Table I

	COSTS				
	Capital	Land	Operating	Energy	Recoverability
Biological	○	●	○	○	none-presently
Wet Oxidation	●	○	●	?	Energy
Air Oxidation	◒	○	●	●	Energy
$KMNO_4$	◒	○	●	○	No
O_3	●	○	◒	●	No
H_2O_2	○	○	◒	○	No
Electrolytic	◒	○	●	●	No
Incineration	●	○	●	●	heat-possibly

○ = low ◒ = medium ● = hi ? = uncertain

Table II

EPA Demonstrations of Biological Treatment

Grantee Site	Project No.	Waste Character	System	Comments
Armak, Inc. McCook, IL	12020 EFW	Fatty acids and derivatives	Activated Sludge (0.5 mgd flow)	Odor problem required covering aeration basin. Resultant temp. increase caused problem with floc character. 90% Reduction in hexane solubles achieved.
Sodyeco Charlotte, N.C.	12020 GIZ	Disperse dyes, organic chemicals	Activated Sludge and separate biological decomp. of thiosulfate; DAF. (2.2 mgd flow).	Good color, SS removal, problems overcome in thiosulfate treatment. Avg. % removal BOD_5 = 90+% Na Thiosulfate = 99%
S. B. Foot Tanning Redwing, Minn.	12120 DSG	Side leather tanning	Aerated lagoon; sludge incineration (2.1 mgd flow)	Effluent to be reused in tanning operation.
Melbourne Water Sci. Inst., Victoria, Aust.	12060 EHS	Fruit & Vegetable cannery wastes	Anaerobic lagoon followed by oxidation ditch.	Anaerobic lagoon removed 75-80% of BOD. Oxidation ditch further reduced BOD to low levels was found to be highly stable to overloads.
John Morrell & Co. Ottumwa, IO	12060 EUB	Packing house	Multiple oxidation channels (ditches); 3.5 mgd flow.	
Amer. Dist. Co. Pekin, IL	12060 FLL	Distilling waste	Comparison of activated sludge & biodisc. Act. Sludge: 90% BOD_5 removal; Biodisc: 90% BOD_5 removal.	Biodisc capacity had to be downrated to achieve 90% BOD_5 removal. Act. Sludge proved more economical, consistent and able to handle shock loads. Final report available. 660/2-74-014.
City of Macon Macon, Georgia	12130 DPD	Domestic plus Kraft linerboard	Pilot comparison of extended aeration with plastic media trickling filter plus subsequent aeration.	BOD removal averaged 92%. Sludges difficult to dewater. High Cl_2 requirement for disinfection.
Goodrich Chem. Pedricktown, NJ	12110 DJI	PVC polymerization wastes	Activated Sludge & polishing pond 0.85 mgd flow.	BOD_5 removal 78.5%.
Firestone Tire & Rubber Lake Charles, LA	12110 GLP	Synthetic rubber mfg. wastes.	DAF & aerated lagoon. 3.55 mgd flow. % Removals: BOD_5, COD 84%; SS 85%.	Found more effective than EGD BPT requirements. Cap. Cost: $1.5 million. Total op. cost 50¢/1000 gal. Final report avail. 660/2-73-018.
Black & Decker Hampstead, MD	WPD-117	Combined industrial, sanitary.	Oxidation pond for polishing.	Water recycle achieved. Final report available.
Beaunit Fibers Etowah, Tenn.	12090 PCO	Nylon 66 mfg.	Act. Sludge, using excess O_2 in off gas stream from mfg.	Water Qual. Standards require 92% BOD_5 removal.
Cone Mills Greensboro, NC	12090 HLO	Textile Finishing wastes	Activated carbon catalyzed activated sludge-PACT.	Stream water qual. standards require 92% BOD_5, 98% COD, 96% SS removal. Final report available 660/2-74-039.
Crown Zellerbach Lebanon, OR	12100 ELW	Sulfite Pulping wastes	Aerated Lagoon.	80% BOD removal. Annual operating cost $169,500.
Klamath Plywood Co. Klamath Falls, OR	12100 EZU	Plywood Glue wastes (urea/CH_2O)	Activated Sludge; 8000 gpd flow. P addition required, increased BOD removal from 30% to 78%.	Act. Sludge found not to be sufficient. Cold weather adversely affected efficiency.
DuPont Deepwater, N.J.		Complex organic chem. mfg.	PACT system 43 mgd flow.	Just on stream 12/76.

used[5]! If the COD BOD_5 ratio is high (>4/1) in the raw waste, the residual COD will frequently remain high in the final effluent as well and may not satisfy Federal or State requirements. Whether such a "treated" waste is acceptable for discharge will depend on the actual level, the nature of the pollutants, and the assimilative capacity of the local receiving body of water, i.e., water quality criteria. In view of the current EPA emphasis on chemical toxicity[2, 6] biological systems may be hard-pressed to achieve acceptable effluent qualities in the coming years without significant support from other "polishing" treatment. When such post-treatment must be incorporated to meet discharge requirements, assure consistent operation, or as pretreatment for municipal systems, a determination of total capital costs (BPT plus BAT) will often suggest other alternatives as equally cost-effective. This will become most significant in satisfying those 1983 BAT requirements where specific "toxic" pollutant control will be a major factor.

As activated sludge systems have largely replaced the trickling filters of past decades, particularly for industrial wastes, several adaptations of the activated sludge process are now being introduced to minimize land requirements, accelerate degradation (or throughput) rates, increase the rate controlling oxygen uptake, etc. Some of these systems are indicated in Table III. No at-

Table III
Adaptations of Activated Sludge Biological Treatment

Modification	Identifying Name	Company
Use of oxygen	UNOX	Linde
		FMC
Increased area volume	Biodisc	Autotrol, others
	Biodrum	Carborundum
Improved oxygen distribution	HYFLO	Ecolotrol
	Betzaerator	BETZ
	Forced Free Fall oxygenator	Airco
Pollutant or waste-specific bacteria	—	Biopac
Accelerants	PACT	DuPont
	H_2O_2	FMC, DuPont

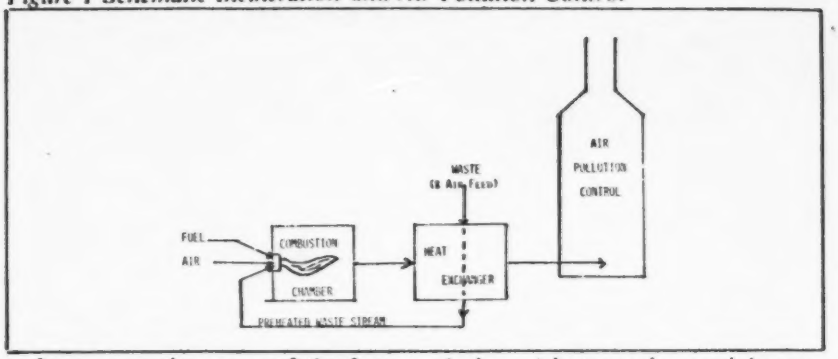
tempt has been made to include all proprietary systems nor is the omission of a system meant to reflect on its utility; rather the Table is intended only to make the reader aware of some of the improvements and modifications that are under development.

Air Oxidation

Non-biological oxidation with the oxygen in air has been in use for many years as an "ultimate" method for destroying wastes of particularly refractory chemical or physical nature, for the destruction of air entrained pollutants, and for the elimination of sludges and other solid wastes. In air pollution control, oxidation has had particular success for deodorization, such as the removal of hydrogen sulfide. However, such specific oxidations have been less widely used in wastewater treatment; instead the approach has been to partially or totally degrade the pollutants under extreme thermal conditions. In its simplest, most common form, this process is, of course, incineration. Where partial oxidation is employed, it is then followed by a conventional biological treatment.

Incineration has been used to destroy everything from biological treatment sludges to solid wastes (animal carcasses, boxes, cartons) to toxic liquid wastes. It has been used for the vapor phase oxidation of gaseous pollutants and for the elimination of contaminated solvents. While relatively simple in concept, incineration systems must address a wide range of problem areas in practice. And, now, with concern over energy supplies, the need for an external fuel must be considered prominently. Although the energy penalty may be negligible when "burning" solid combustible wastes or high concentrations of combustible liquid wastes which can supply much of the needed energy, the same cannot be said for dilute wastes such as those which are the primary topic of this paper. Not only must supplemental energy be supplied to oxidize the waste, constituents but, more important, considerable energy is required to heat and vaporize the solvent water, and then raise it to oxidizing conditions (1500°F or more). Evaporating one pound of water requires 970 Btu. Even at 1000 ppm concentration, the typical organic pollutant would only supply a small portion of the needed energy.

Figure 1 Schematic Incineration and Air Pollution Control



Let us examine some of the factors inherent in the use of incineration for the elimination of 'relatively dilute) industrial wastes. It is usually accepted that temperatures of at least 1500°F and residence times of at least 0.5 seconds are necessary and adequate to oxidize completely most organic compounds.[7] Proper fuel, air and waste injection systems are met. Materials of construction are often a problem due to temperature and inherent corrosive nature of the existing conditions. To prevent contamination of the atmosphere, complex and costly emission control and air cleaning systems are required. Scrubbers and particulate removal devices (electrostatic precipitators and/or bag filters) are customarily needed to trap partially oxidized volatile organic acids, ash fines and metallic fumes, all of which must themselves be disposed of subsequently. Recovery of waste heat has not been the usual practice but there is now a trend in this direction (see Figure 1).

EPA's Office of Research & Development (ORD) has had and currently has several projects underway in which incineration of solid or liquid wastes is being considered. One which is of particular relevancy to this paper is a combined evaporator and fluidized bed incinerator being developed at the Pfizer Phar-

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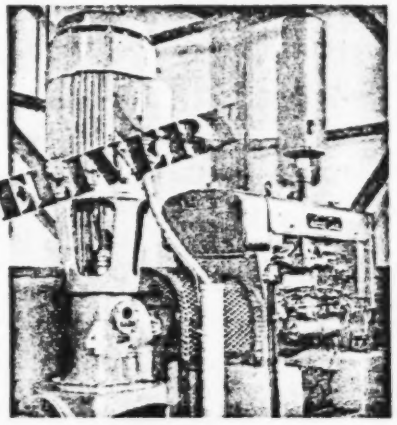

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maceutical Co. facilities in Barceloneta, Puerto Rico.[9] Preliminary calculations indicate that under ideal conditions this system will destroy the liquid organic wastes and contribute useable and useful steam to the manufacturing facilities.

Evaporative concentration and incineration of wood pulping liquors (wastes) has long been an accepted means of eliminating serious pollution sources, while generating process steam and recovering caustic for reuse. Approximately 35.50% of the energy used in the pulp industry is derived from waste.[9] [10] In an EPA co-funded project at Mandan, North Dakota, the American Oil Company (12050 EKT) has evaluated a fluidized bed incinerator for the disposal of caustic and oily sludge generated at a refinery.[11] Due to problems in the fluidized bed, extensive design modifications were necessary. In another study, carried out for EPA by the Ohio Department of Natural Resources by Battelle,[12] it was demonstrated that various industrial wastes and sludges could be incinerated in a fluidized bed incinerator "without generating noxious exhaust gases."

In a widely publicized EPA project, the disposal of organo-chlorine wastes by incineration at sea aboard the incinerator ship Vulcanus was evaluated.[13] It is reported that more than 99.9% of the wastes were oxidized and that there was no measurable increase in the concentration of trace metals or organic chlorides in the water or marine life. Ocean incineration appears, based on these results, to be a viable alternative for disposal, particularly for wastes which are not readily and economically treatable by conventional processes nor safely disposed of by more commonplace routes such as deep well injection or ocean disposal, which themselves are not highly desirable.

Some years back, Barber Coleman introduced a system called "Wet-Ox" in which aqueous organic wastes could be oxidized in the liquid phase using a combination of elevated temperature and pressure. Although Barber Coleman is no longer active in this business, a variation of the concept has been commercialized by Zimpro, Inc. in their wet oxidation system.[14] Parallel work also is being carried out in Europe.[15] The use of a liquid phase, pressured reaction minimizes many of the energy, exhaust gas, and corrosion problems inherent in incineration. Energy consumption is minimal and, at the pollutant concentration for which the process is considered most viable (>15000 ppm of COD), the process may become autogenous and actually generate usable energy. Neither the energy required for vaporization of water nor that needed for raising the vapor temperature to 1500°F is needed. Typically, only some 560 Btu./gallon (70 Btu/lb.) are required to be added for wet air oxidation, as opposed to 20,000 Btu/gallon for incineration of the same waste.[14] Similarly, because the system is under pressure and closed to the environment, air pollution problems (and control needs) are minimized and most pollutants are retained in the liquid phase. The severity of reaction conditions are, however, such that materials of construction still are a major cost factor; titanium vessels are often necessary and this contributes significantly to the high capital cost for wet air oxidation.

Figure 2 Wet Air Oxidation

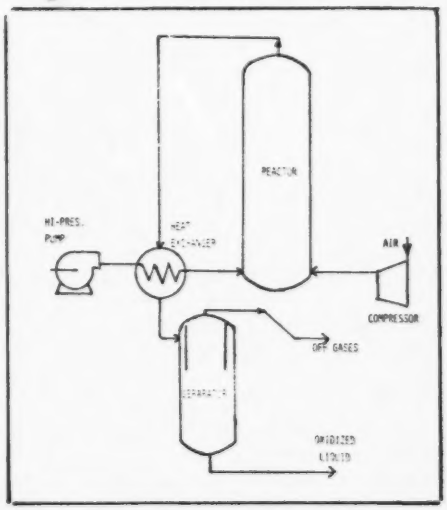


Figure 3 Use of Wet Air Oxidation for "PACT" Sludge Treatment

Because the wet air oxidation process is not inexpensive, it has found primary use as a "pretreatment" for oxidizing BUT NOT TOTALLY DESTROYING relatively concentrated solutions of dissolved organic pollutants and thus increasing the amenability of the contaminants to more conventional treatment such as biological processes. By virtue of its insensitivity to the chemical (toxic) nature of waste, wet air oxidation can be of value in degrading complex toxic chemicals which can not be treated directly by conventional biological systems. Wet air oxidation has been used for a variety of wastes, including pulping wastes, acrylonitrile liquors, etc.[14]

The relatively severe temperatures and pressures normally required for wet air oxidation have led to the development of both heterogeneous and homogeneous catalysis (e.g., copper) systems which allow a significant reduction in the severity of reaction conditions. Today, catalysts are widely used in wet air oxidation systems. The process is also finding application as a means of breaking down biological sludges and in regenerating powdered activated carbon such as that recovered from the duPont "PACT" system.[16] Figure 3.

The long term goal of air oxidation systems would, of course, be low or ambient temperature and pressure, liquid phase systems. Although this goal is still a long way from achievable (most organics oxidize slowly, if at all, under such mild conditions), work is being carried out, particularly in the area of homogeneous and heterogeneous catalysis, to reduce the require-

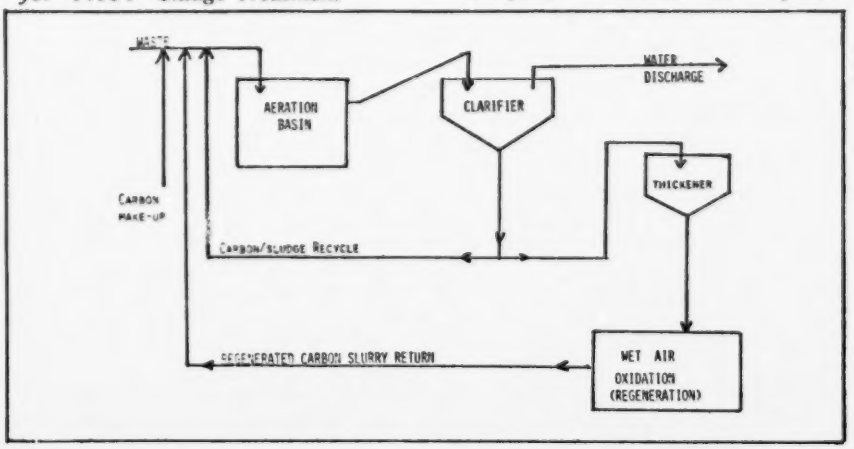


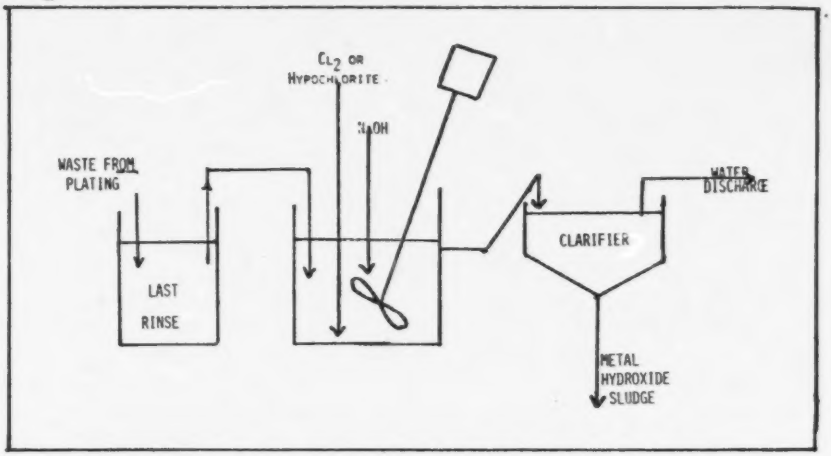
Table IV

Sample Waste Treatment Costs[1]

Process	Cat. Cracker wastewater[2] ¶=1000 gal.	Coke Plant wastewater[3] ¶=1000 gal.
Oxidation Pond	0.14-0.51[4]	0.14
Activated Sludge	0.24	0.24
Activated Carbon	0.50-0.86	2.80
Ion Exchange	1.02	3.02
Wet Oxidation	1.00	0.81-1.16
Aqueous phase catalytic oxidation	0.57	0.24-0.75

[1]See Katzer, Ref. (20) for more complete data
[2]700 mg 1 phenol
[3]4000 mg 1 phenol
[4]Costs are all adjusted to early 1974

Figure 4



ments below those required for wet air oxidation. In a recent EPA funded project at the University of Delaware,[17] some success has been obtained at less severe conditions with phenol and heterogeneous catalysts. However, the applicability to real industrial wastes has not been as successful. Poisoning of the catalyst, mechanical instability, and leaching of metals into the wastewater remain unresolved problems. A number of other research programs have also been supported by EPA's ORD in liquid phase catalytic oxidation[18, 19] over the past years.

Relative treatment costs for two specific, real wastes have been presented by Katzer, and are shown in Table IV.[20]

One unique application of catalytic oxidation under ambient conditions is in the advanced development and commercialization phase. The Calgon Co. has described a process for oxidation of cyanide ion in which the aqueous solution is passed through a carbon column along with an air or oxygen stream. Copper ion is introduced in a separate side stream, as the catalyst.[21] EPA is currently involved in a closely related project using CN bearing petroleum refinery wastes and powdered carbon.[22]

Chemical Oxidation

Primary among the chemical oxidants that must be considered is chlorine. Used either as gaseous or liquid chlorine or as hypochlorite ion to generate nascent oxygen atoms by the reaction:

$$Cl_2 + H_2O \rightarrow 2HCl + O,$$

this approach finds broad, international use for disinfection of drinking water and as the final treatment for wastewaters. (Whether nascent oxygen is the active species in all cases is uncertain. Alternatively, OH radicals may be the active oxidizing species in chlorine, ozone, peroxide and some electrochemical oxidation.) The oxidation of carboxylic acids with chlorine has also been demonstrated in a 200 gpm waste brine stream by DOW.[23] Reaction effectiveness was found to be improved significantly by the use of ultraviolet light catalysis and careful pH control. Other instances of UV catalyzed oxidations with chlorine have also been documented.[24]

Because of its safety requirements, the use of gaseous or liquid chlorine is usually limited to large facilities with the hypochlorite route being more common at smaller sites. In either case, the chemical cost is far from insignificant (recently estimated at 80¢/lb. of COD removed). In addition, within recent years serious questions have arisen concerning the possible generation of more hazardous chlorinated byproducts during the treatment; for example, it has long been known that chlorophenols are or can be produced by chlorination of phenol in a waste stream. The increased ease with which this material is detected by taste has long made this a problem.

Alkaline chlorine (or hypochlorite) has been and remains the principal treatment method for cyanide ion destruction.[25] Depending on reaction conditions (temperature, time, Cl_2 concentration and pH) the reaction can be carried all the way to carbon dioxide or can be discontinued at the cyanate intermediate. EPA has supported several projects to demonstrate this base-line technology and some improved techniques for its use. See, for example, EPA's project with the S.K. Williams Co.[26] in which chlorine (or hypochlorite) treatment is integrated into the rinsing operation. The heavy metal counterions are precipitated simultaneously as the hydroxides or oxides under the alkaline conditions of oxidation. (Figure 4.) Many different configurations now exist for this process. In situ generation of chlorine or hypochlorite by an electrolytical process has been documented as one of the newest approaches.[27] Although chlorine is quite effective for free cyanide and many of the metal cyanide complexes used in metal treating and electroplating, it is not effective for certain highly stable metal cyanide complexes (e.g., Fe, Ni).[28] These complexes require much more severe conditions of oxidation to achieve breakdown.

Ozone has long been recognized as a very strong oxidant of organic chemicals, and has found wide use in synthetic chemistry, particularly to cleave unsaturated bonds. Until recently, however, the cost of generating ozone has been too great to allow use of this technique for anything but the final treatment (polishing) of wastewater, for deodorizing industrial gas streams and for treatment of potable waters. Within the past five years or so, significant reductions in the complexity and cost of ozone generating equipment and improvements in generation efficiency have occurred. Further significant improvements in ozone generation are anticipated over the coming 5 to 10 years. This, coupled with concern over chlorine disinfection as a source of toxic chloro-organics, has led to expanded interest in this technique for both more extensive waste treatment and for disinfection of both wastewater and drinking water.[29] Since ozone decomposes only to oxygen there are

no additional, undesirable by-products and final dissolved oxygen is, if anything, increased. Ozone also appears capable of deactivating bacteria and may destroy certain viruses as well.[30] The first sizeable installation for treatment of industrial wastewater of which the author is aware was that for the destruction of cyanide and phenols by Boeing in Wichita, Kansas.[31] Recently, EPA completed a project wherein ozone was used in a small, full scale system to destroy metal cyanides at an electroplating installation.[32] Cyanide levels well below 1 ppm were routinely achieved at a cost comparable to that for conventional alkaline chlorination (Figure 5). Cyanate could be oxidized effectively by using larger doses of ozone. EPA has successfully demonstrated the use of ozone to reoxidize photographic ferrocyanide complexes to ferri-cyanide.[33]

Traditionally, mass transfer of ozone to the liquid phase has been considered the rate controlling factor and much effort has been devoted to improved mixing devices for overcoming this deterrent to effective reactions. However, as with chlorine, certain species, both organics and metal cyanide complexes, remain resistant to conventional ozone treatment. Obviously these reactions are not mass transfer dependent. A new technique, using ozone coupled with low intensity ultraviolet irradiation and, if necessary, elevated temperature, has been developed and found capable of treating a wide range of ozone-resistant wastes and improving the rates of decomposition for many others. For example, iron cyanide complexes resistant to both conventional alkaline chlorination and ozone treatment alone and nitro-bodies such as those present in the "pink water" generated during the manufacture of TNT and toxic to biotreatment can be readily decomposed using the new technique.[34] PCB's and DDT are also readily degraded by these more vigorous conditions.[35]

The use of ozone as a pretreatment for other unit processes is also being examined by various researchers. An EPA funded study at Clemson University[36] will evaluate the biodegradability of highly refractory dye wastes after ozone pretreatment. Similarly, researchers have recently found that ozone pretreatment improves the capacity of

Figure 5. Ozone Treatment of Electroplating Wastes

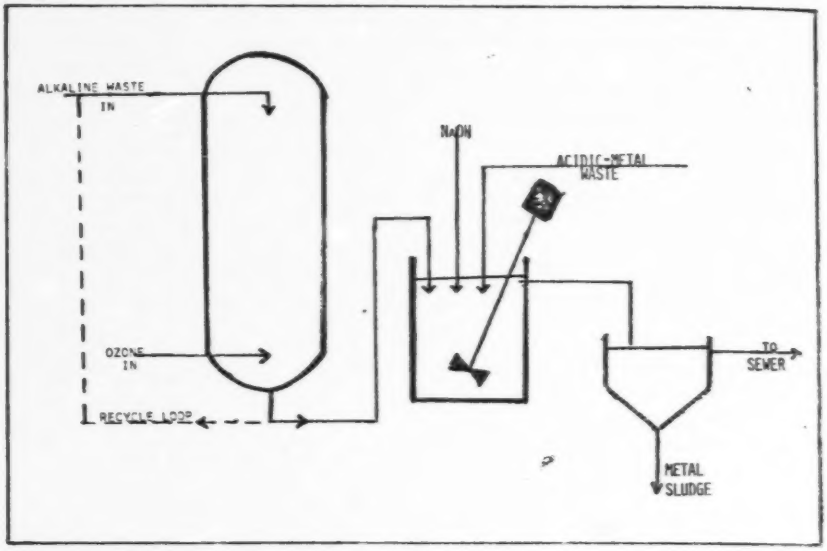


Figure 6. Alkaline Oxidation Pulping

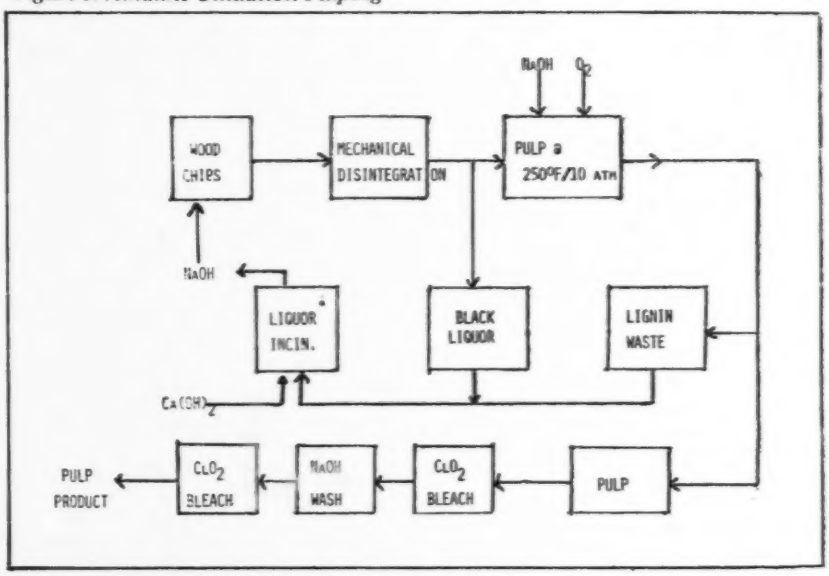
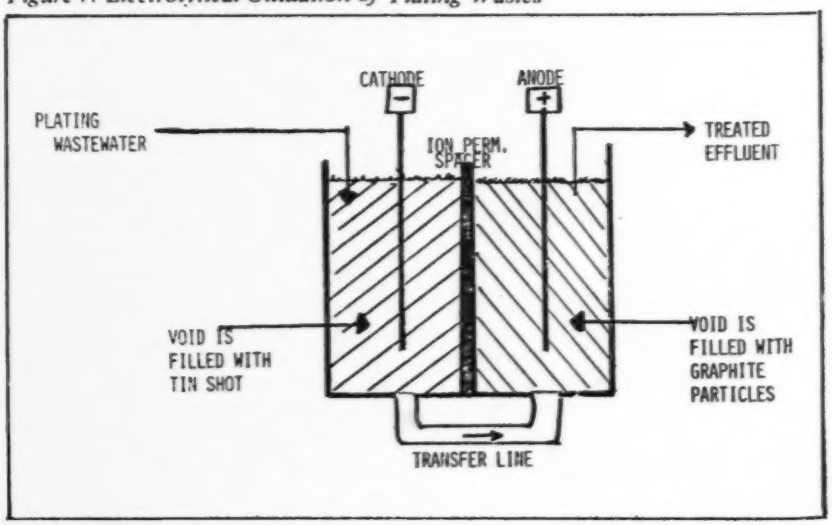


Figure 7. Electrolytical Oxidation of Plating Wastes



carbon adsorption systems and makes possible much longer life cycles.[37] The ultimate value of ozone in either of these uses and the probable mechanism are still to be established.

There is some evidence that the combination of ozone with ultrasonics also improves decomposition rates.[18] The use of catalysts, particularly copper, to accelerate ozone oxidation reactions is extensively documented.[38]

Hydrogen peroxide has occasionally been employed as a primary chemical oxidant for wastes,[39] but cost has usually limited its use in wastewater treatment to that of an accelerant (probably) for biological treatment[40] or for oxidation of specific reactive species such as sulfur compounds in wastes such as those arising in the pulping industry.[41] Metal ion catalysis has been reported to accelerate such oxidations.[42]

The duPont Company also has a cyanide waste treatment system based on a combination of hydrogen peroxide and formaldehyde. This system, called "Kastone" destroys cyanide and precipitates the metals as hydroxides or oxides.[43] EPA has completed an evaluation of this technique.[44] Recently, the use of in situ electrolytical generation of hydrogen peroxide has been proposed as a new, cost effective means of oxidizing organic pollutants.[45] The scope of this technique is yet to be determined. EPA has also participated in a study of a process change involving the substitution of hydrogen peroxide for dichromate.[46] Reduced pollution and cost-effective recovery of a copper oxide sludge were achieved.

Potassium permanganate is a well-known oxidant, but not one which has received widespread attention in the pollution control program.[47] However, potassium permanganate at low levels has been reported to successfully remove soluble iron and manganese and eliminate undesirable tastes and odor from drinking water.[48] Upon oxidation, potassium permanganate is reduced to the highly insoluble manganese dioxide which is easily separated. Its use as an oxidative scrubber for undesirable odors from an industrial waste treatment process has also been considered. Similarly chromic acid, while widely used in synthetic and analytical chemistry (e.g., COD analysis), has not been used to any degree in large scale waste treatment. Some thought has been given in the plating industry to combining chromic acid and cyanide wastes — carefully — to achieve the desired oxidation of CN and simultaneous reduction of Cr (VI). However, the need to maintain conventional treatment systems on stand-by to handle the excess of either waste makes this approach less attractive.

The pulping industry is testing an improved, non-polluting process called alkaline-oxidation in which alkali-softened pulp is treated with oxygen under alkaline conditions to remove residual lignin. (Figure 6.) The black liquor (lignins) is then evaporated and burned as a fuel source. Detrimental chlorides and sulfur-related odors are eliminated.[10]

Electrolytically induced oxidation is a technique that has always interested researchers as a means of introducing an oxidant without adding extraneous chemicals or ions. It has long been accepted as a cost-effective means of destroying concentrated cyanide solutions such as spent plating baths[49]; however, practical adaptation to more dilute cyanide solutions (<100 ppm CN) has only been achieved within the last several years.

EPA has demonstrated that conductive carbon particles can be used to help overcome the high electrical resistance of the dilute solution.[50] The benefits of a short electrical path in overcoming the problem of solution resistance have been demonstrated in another EPA funded project[51] by passing the waste between two narrowly spaced concentric tubes which also serve as the electrodes (Figure 7). Both techniques can successfully reduce residual cyanide to <1 ppm. Some success has also been demonstrated with electro-oxidation of organic pollutants and as a first step in a cheese whey recovery process.[52]

Gamma radiation induced,[53] and visible light induced[54] oxidation have also been explored as innovative potential techniques for destruction of complex organic wastes, particularly those from the textile and pulping industries. Microwave destruction of toxic wastes is now also being developed,[55] but whether this process is "oxidative" is an open question at this time. These processes have not yet attracted great interest and the economics are usually not competitive. In situ electrolytical generation of chlorine has been used to oxidize cyanide wastes from metal finishing and photographic processing, as noted earlier.[27]

Summary

It must be recognized that economics remain a primary driving force in the selection of any treatment system. Specific costs would have little value for plants of different character and size, but Table I does present some cost generalizations for different treatment approaches — which should be used only for general guidance. However, since the oil embargo of October, 1973, energy requirements and their cost have been introduced as a factor of importance. Besides having a wide range of capital-intensities as the treatment systems become more sophisticated, the different systems also require a wide range of energy inputs of different types and potential availabilities. This is only the first reckoning: the use of energy plus an oxidizing agent to cleave bonds of carbon with hydrogen, carbon, nitrogen, etc. to decontaminate industrial process wastes. In the second analysis, oxidation of materials in many of the systems described above could generate energy or make possible, with proper innovation, the recovery of potential energy source materials (fuels) or valuable chemical feedstocks. Development of optimized systems over the coming years will allow the most effective and efficient selection and integration of biological, chemical and thermal oxidative techniques in treating industrial wastewaters and meeting current and anticipated regulations such as those mandated by PL-500. Research is still needed on those techniques now in use or being developed to delineate and expand their areas of applicability and to develop new and most cost-effective control process concepts and equipment. Caution and safety must always be a prominent factor when using oxidative systems. To encourage such work and accelerate the development of improved methodology, the Clean Water Act (PL-92-500) and predecessor laws have authorized EPA, as one of its missions, to support pertinent research, development and demonstration grants such as those referred to throughout this paper.

It must also be kept in mind that oxidative processes cannot and will not operate in a vacuum. More realistically, such processes will be used in conjunction with a variety of other techniques which destroy pollutants by non-oxidative routes; allow separation and/or concentration of wastes (e.g., reverse osmosis, carbon adsorption, ion exchange, evaporation, etc.); and achieve more economical removal of pollutants by physical-chemical treatment with lime, alumina, or polyelectrolytes. Process modifications which segregate wastes into groups which can most effectively and economically be treated by any of the above approaches or make possible the recovery of valuable resources and the generation of fuel materials or thermal energy will play an increasing role in industrial pollution control over the coming years.

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